

Chitosan Nanocoating on Cotton Textile Substrate Using Layer-by-Layer Self-Assembly Technique

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ABSTRACT: An attempt was made to deposit a nanocoating onto a cotton textile substrate using a layer-by-layer self-assembly approach. Chitosan, a natural biopolymer with polycationic characteristic, was used as a polyelectrolyte along with poly(sodium-4-styrene sulfonate) as an anionic polyelectrolyte for the first time on a textile substrate using this technique. The nanocoated surface was evaluated for surface characteristics such as the contact angle and scanning electron microscopy. The effect of ultrasonication during the intermediate washing steps was explored. Ultrasonication during the washing steps clearly

helped in depositing more uniform bilayers onto individual fiber surfaces; this contrasted with the deposition of a continuous coating layer, which was nonuniform and had a lot of surface cracks. The use of this novel method for depositing chitosan onto cotton imparted antimicrobial properties to the fabric without adversely affecting its flexibility, feel, or breathability. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2793–2799, 2011

Key words: nanocoating; electron microscopy; cotton fibre; layer-by-layer; self-assembly

INTRODUCTION

A nanocoating is a deposition of matter on the surface of a substrate that conforms to certain characteristics with respect to uniformity and feature size. The thickness of a nanocoating is generally less than 1 μm ; this contrasts with conventional coatings on textiles, which mostly have thicknesses in the micrometer or millimeter range. Recently, much work has been focused on the application of nanocoatings to different materials that are not necessarily textiles. A nanocoating provides control over the surface and interface properties at a molecular level, and therein are the differences and advantages of nanocoatings versus conventional coatings.

The modification of textile materials by either finishing or coating is widely used to enhance their quality and add functionality or properties such as wrinkle resistance, improved color or light fastness, flame retardancy, water or oil repellency, and even antimicrobial properties.^{1,2} However, conventional coatings, which are approximately micrometers to a few millimeters thick, can make fabrics totally impermeable, and this adversely affects the handle, feel, and breathability. Thus, nanocoatings on individual fiber surfaces, which are submicrometer in

their thickness, are expected to impart properties to fabrics without affecting their handle or breathability. The nanocoating of textile materials is a relatively new field, and popular techniques that have been reported include plasma-assisted polymeric coating^{3,4} and layer-by-layer (LBL) or self-assembly approaches.^{5–8}

The LBL process is based on the alternate deposition of charged cationic and anionic polyelectrolytes to create nanolayers on material surfaces.^{9–11} This polymeric multilayer (PEM) self-organization process was first reported by Decher's group in the early 1990s.⁹ PEM films created via LBL deposition were later used to modify the surface properties of materials in electronic products, machinery tools, and medical devices and implants.¹² PEM films have mostly been deposited onto flat surfaces such as silicon, metal, glass, and quartz slides for a range of applications, such as superhydrophobic, antimicrobial, and catalytic applications.^{13–15}

However, the application of the LBL process to the modification of the surfaces of textile substrates (i.e., fibers or fabrics) has not been extensively studied and is not well understood. Recently, there have been a few reports on the deposition of nanolayers of polyelectrolytes onto cotton,⁵ silk, and nylon fibers.^{6,7} Hinestroza and coworkers⁵ demonstrated the feasibility of using the LBL deposition process on cotton substrates with poly(sodium-4-styrene sulfonate)(PSS) and poly(allyl amine hydrochloride)(-PAH), and they observed that the process is more

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dependent on the nature of the polyelectrolyte rather than the nature of the original substrate. Dubas and coworkers reported use of the LBL deposition method to immobilize silver nanoparticles on nylon and silk fibers⁶ and to improve the color fastness of silk against washing and rubbing.⁸ Park et al.¹⁶ reported the alternating deposition of alginic acid salt and chitosan on nylon 6 fibrous mats with the LBL technique. Krogman et al.¹⁷ used a nonwoven mesh of nylon fibers made by electrospinning for the alternating deposition of different polyelectrolytes or nanoparticles. For this deposition, they used an LBL vacuum-assisted spraying technique. Lin et al.¹⁸ used aqueous dispersions of clay nanoplatelets and poly (diallyl dimethylammonium chloride) to modify the surfaces of lignocellulosic fibers with the LBL technique. In a U.S. patent, Jamshid¹⁹ described a special pretreatment of the fabric substrate to activate it and make it suitable for the subsequent application and strong attachment of a conductive coating with the LBL technique.

In this article, we report the nanocoating of a cotton fabric substrate with the LBL process; PSS was used as the anionic polyelectrolyte, and chitosan, a natural biopolymer, was used as the cationic polyelectrolyte. By either padding or exhaust methods, chitosan has been extensively used as a finishing agent for textiles to impart antimicrobial properties on account of its polycationic nature.²⁰ However, the nanocoating of woven cotton fabrics with chitosan as a polyelectrolyte by the LBL technique is being reported here for the first time. Additionally, an ultrasonication-assisted washing step in distilled water was introduced after each dip in the polyelectrolyte to ensure the complete removal of loosely adhering polyelectrolyte layers, and its effect on the uniformity of the nanocoatings on the fabric substrate was investigated with scanning electron microscopy (SEM). The nanocoated fabric samples were further tested for contact-angle measurements, air permeability, and antibacterial properties.

EXPERIMENTAL

Materials

A 100% cotton fabric with a plain weave (110 gm⁻²) that was previously scoured, bleached and mercerized was used as the substrate for the nanocoating. PAH and PSS, both having a molecular weight of 60,000, were procured from Sigma-Aldrich (Steinheim, Germany). Sandene 2000, an aliphatic polyamine and cationizing agent (M/s Clariant, Mumbai, India), was used to create positive charges on the cotton surface. Chitosan (molecular weight ~ 140 kDa) was procured from Sigma-Aldrich. All chemi-

cals were used as received without any further purification or treatment.

Deposition of the polyelectrolyte multilayer film on the cotton substrate with the LBL process

Activation of the cotton surface

The cotton fabric was treated with Sandene 2000 at a concentration of 4% (v/v) with a material to liquor ratio (M/L) of 1 : 20 for 20 min at 50–60°C. The samples were dried at room temperature before further layers were deposited.

LBL deposition

The cationized cotton fabric was alternately dipped into a 1% (w/v) PSS aqueous solution and a 1% chitosan solution (prepared under mildly acidic conditions by the addition of 10 mL of acetic acid) for 5 min at room temperature. The samples were washed in distilled water for 5 min after each treatment with a polyelectrolyte solution before they were immersed in the oppositely charged polyelectrolyte solution. This process sequence was repeated for the deposition of up to 20 bilayers. Small fabric samples were removed after the deposition of each bilayer. Alternatively, experiments were also carried out in which washing in distilled water was assisted by ultrasonication after the deposition of each polyelectrolyte.

SEM analysis

The nanocoated and uncoated samples were coated with silver and examined with a Zeiss EVO 50 scanning electron microscope (Cambridge, UK) operating at an accelerating voltage of 0.3–30 kV.

Contact-angle measurements

The contact angles of the fabric samples were measured with a Kruss K100 tensiometer (Hamburg, Germany).

Air-permeability testing

Air-permeability tests were conducted for both treated and untreated cotton samples using a Textest AG, FX 3300 LABOTESTER III (Schwerzenbach, Switzerland) at 100 Pa.

Antimicrobial-activity testing

All the materials used for antimicrobial testing (e.g., liquid culture, solid culture, microtips, and distilled water) were sterilized under standard conditions (i.e., 120°C, 15 psi, and 30 min) before use.

The unwashed and washed samples were subjected to the modified colony counting method (AATCC Test Method 100-1999) for the evaluation of the antimicrobial activity of the nanocoated fabric. With the colony counting method, a prepared fabric swatch (1" × 1") was placed in a sterilized flask containing a liquid culture solution [5 g/L peptone and 3 g/L beef extract (pH = 6.8 ± 0.1) at 25°C]. The flask was shaken for 24 h at 150 rpm on a laboratory shaker to release the bacteria from the swatch. After 24 h of incubation, serial dilutions of the liquid were made in sterilized water. Dilutions of 10⁻³, 10⁻⁴, 10⁻⁵, and 10⁻⁶ were used for the colony counting method. One hundred microliters was spread on the agar plate [5 g/L peptone, 3 g/L beef extract, and 20 g/L agar (pH = 6.8 ± 0.1) at 25°C], and the plates were incubated at 30°C for 24 h. After incubation, the bacterial colonies were counted. The reduction of the number of colonies (%) in the treated sample was compared to the untreated sample to determine the antibacterial activity of the fabric:

$$\begin{aligned} \text{Antimicrobial activity or reduction percentage} \\ = [(A - B)/A] \times 100 \end{aligned}$$

where *A* is the number of bacterial colonies on the untreated fabric and *B* is the number of bacterial colonies on the treated fabric.

Fabric washing

The finished fabrics were washed in a Launder-O-Meter (R.B. Electronic & Engineering Pvt. Ltd., Mumbai, India) according to AATCC Test Method 124-1975 (test IIA) with a nonionic detergent (Lissapol N).

RESULTS AND DISCUSSION

The deposition of multiple ultrathin layers on cotton surfaces by the LBL technique is an arduous task in comparison with planar substrates such as films because textile fabrics are flexible and porous and have a highly uneven surface to start with. For the first time, we explored the use of chitosan as a cationic polyelectrolyte with PSS as a complementary anionic polyelectrolyte. For comparison, an initial set of fabric samples was coated LBL with PAH and PSS as oppositely charged polyelectrolytes, and 1, 6, 8, 10, 12, 13, 14, or 15 bilayers were deposited with the LBL deposition technique.

Contact-angle measurements

The deposition of increasing numbers of bilayers of polyelectrolytes on the cotton fabric modified its sur-

face characteristics, which were expected to affect its contact angle and surface energy. The presence of noncontinuous coatings with up to six bilayers initially was further confirmed by changes in the contact angle with the addition of each bilayer. However, after the deposition of more bilayers, the coating became continuous enough, and no change in the contact angle was observed after the further addition of bilayers. Thus, the contact angle was affected by both the roughness and the composition of the surface. The contact angles of the nanocoated fabric were expected to lie between those of the uncoated fabric surface and the coating material (i.e., the polyelectrolyte). As the number of bilayers increased, the properties of the coated fabric were expected to become similar to the those of the coating material (i.e., the polyelectrolyte rather than the uncoated fabric).

Theory

The contact angles of the samples coated with different bilayers were calculated by the sorption method because this method is suitable for materials that absorb a liquid on account of a capillary effect. The basic principle is explained next.

Principle of measurement

To measure the contact angles of solid samples, first the capillary constant of the fabric with *n*-decane as the reference liquid [(CC)_D] was determined because *n*-decane yielded a contact angle of almost zero and thus facilitated further calculations. Subsequently, the contact angle of the solid surface was determined with the instrument's inbuilt software. For contact-angle measurements, a sorption method based on the modified Washburn equation²¹ [eq. (1)], which is applicable to capillaries, was used:

$$l^2/t = (\sigma \cdot r \cdot \cos \theta / 2\eta) \quad (1)$$

where *l* is the flow front, *t* is the flow time, σ is the surface tension of the liquid, *r* is the capillary radius, θ is the advancing angle, and η is the viscosity of the liquid.

To measure the contact angle with water, first a measurement with an optimally wetted liquid (*n*-decane) was carried out, and this produced $\cos \theta = 1$. Therefore, for measurements, first (CC)_D was determined, and for the same sample, the capillary constant with water as the wetting liquid [(CC)_w] was obtained. *r* (used for the bulk powder) was replaced by the quantity *cr*, which describes the orientation of the microcapillaries and the mean radius present in the fabric.

The Washburn equation for *n*-decane is as follows:

TABLE I
Contact-Angle Data for Different Fabric Samples with
Water as the Wetting Medium

Fabric sample	Contact angle (°)
Neat cotton	18
Cotton treated with Sandene 2000	25
Cotton with 1 bilayer	32.3
Cotton with 6 bilayers	62.5
Cotton with 8 bilayers	88.9
Cotton with 10 bilayers	89.7
Cotton with 12 bilayers	89.8

For all the samples, $(\cos \theta)_D$ was 1.

$$l_D^2/t_D = (\sigma_D \cdot c_D \cdot r_D \cdot \cos \theta_D / 2\eta_D) \quad (2)$$

where subscript D represents n -decane. Because l could not be determined directly, it had to be calculated from measured increases in the weight (m), the liquid density, and the tube diameter. l^2 could therefore be replaced by m^2 , so eq. (2) became

$$m_D^2/t_D = (\sigma_D \cdot c_D \cdot r_D \cdot \cos \theta_D / 2\eta_D) \quad (3)$$

The Washburn equation for water is

$$m_w^2/t_w = (\sigma_w \cdot c_w \cdot r_w \cdot \cos \theta_w / 2\eta_w) \quad (4)$$

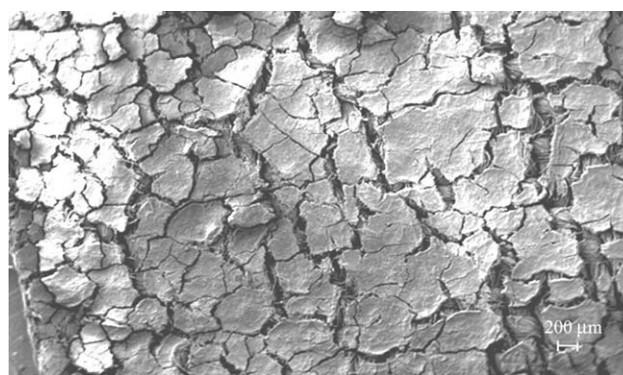
$$\cos \theta_D / \cos \theta_w = (CC)_D / (CC)_w \quad (5)$$

where subscript w represents water. With this equation, the contact angle for any liquid could be obtained. The relationship between the height of the water column (h), σ , θ , the density (ρ), the acceleration due to gravity (g), and r was determined as follows:

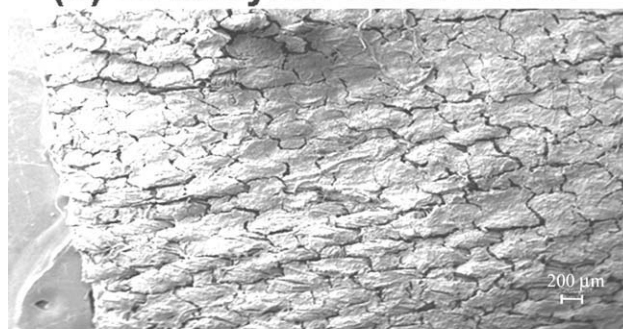
$$h = (2\sigma \cdot \cos \theta / \rho \cdot g \cdot r) \quad (6)$$

Contact-angle analysis showed that the contact angle of the LBL coated fabric with PSS/PAH bilayers increased as the number of bilayers increased up to eight bilayers and thereafter became stable; no significant changes in the contact angle were seen with further increases in the number of bilayers. This may be explained as follows. With the deposition of up to eight bilayers of PSS/PAH, the surface properties of the fabric were completely dominated by the properties of the coating material, and no further changes in the surface properties were expected, except for changes in the coating thickness (Δr), when more bilayers were deposited via the LBL process onto the fabric. In that case, as per eq. (6), only a change in r , which is generally in the micrometer range for fabrics, could change the contact angle with an increase in the number of bilayers. However, θ remained the same despite the increase in the number of bilayers beyond eight

(Table I). This clearly indicates that Δr was negligible in comparison with r , which was in the micrometer range ($\Delta r \ll r$). Therefore, it can be argued that the coating thickness of the LBL deposited bilayers was much lower than the micrometer range and was moving toward the nanorange (<1000 nm). Besides, it also shows that the surface of the fabric was slowly acquiring the properties of the coating materials (i.e., the polyelectrolytes PSS and PAH). The uncoated cotton was highly hydrophilic and had a very low contact angle (10 – 20°) with water, but coating samples with PSS and PAH was expected to make them less hydrophilic, so an increase in the contact angle with water as the wetting medium was observed.



(a) 20 bilayers of PSS/PAH



(b) 10 bilayers of PSS/PAH



(c) 5 bilayers of PSS/PAH

Figure 1 SEM images of LBL coated cotton fabric surfaces with different numbers of bilayers without ultrasonication (125 \times).

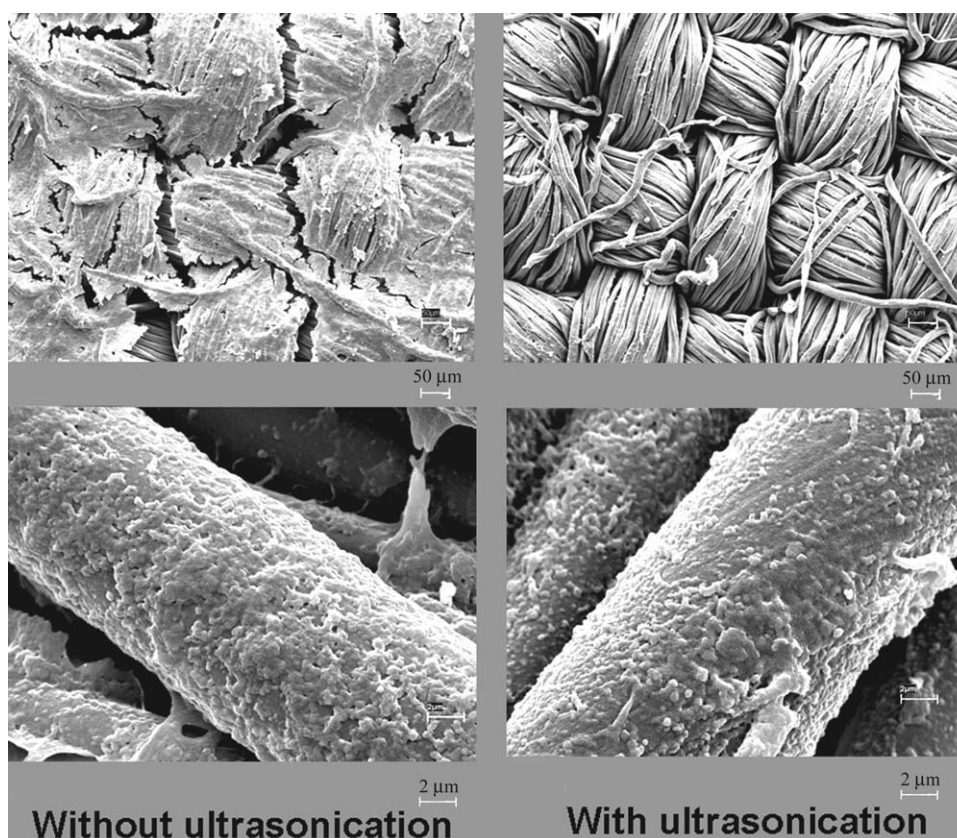


Figure 2 SEM surface images of LBL coated cotton (13 bilayers).

SEM analysis

SEM was used to investigate the effect of increasing the number of bilayers on the fabric surface. Surface images of nanocoated fabrics at a lower magnification with increasing numbers of PSS/PAH bilayers without the use of ultrasonication in the intermediate washing step are shown in Figure 1(a–c). The coated layers on the fabric surface started to show cracks with the deposition of 5 bilayers; the cracks became more pronounced and the surface became rough as the number of bilayers increased up to 20 bilayers in the absence of ultrasonication. Figure 2(a–d) shows PSS/PAH-coated fabric samples with the deposition of 13 bilayers with and without the use of ultrasonication in the washing step at both higher and lower magnifications.

Figure 2 shows that with ultrasonication during the intermediate washing step, a uniform deposition of bilayers on individual fiber surfaces was formed. The loosely held polyelectrolyte layers were removed in a more efficient way with ultrasonication as a tool in the intermediate washing step. There were also apparently no cracks on the coated fabric surface, and very uniform and truly fine bilayers were deposited onto the individual fiber samples in contrast to the samples without ultrasonication. The

cracks on the unsonicated surface were due to the excessive deposition of chitosan and PSS on the entire fabric surface, at the interstices of the fabric, and between two yarns or fibers. Because of the porous nature of the fabric, the coating started to show cracks along the interlacings of the warp and weft threads in the woven cotton fabric. It is also clear that as the number of bilayers increased, the deposition of polyelectrolyte layer on the fibre surface became more nonuniform because of agglomeration, as shown in Figure 3 at a higher magnification.

Air permeability

Air-permeability data (Table II) show that the permeability was marginally reduced in 10-bilayer samples nanocoated with the LBL technique. On the otherhand conventional coating of a polyelectrolyte and poly(vinyl alcohol) (7%) polymer solution about 0.1 mm or 100 micron thick, drastically reduced the air permeability across the fabric because it formed a continuous film, covering almost the entire surface of the fabric, and blocked all porosity through which air could pass. This further indicates that the LBL technique produces ultra thin coatings on the individual fibre surfaces without blocking the pores of the fabric.

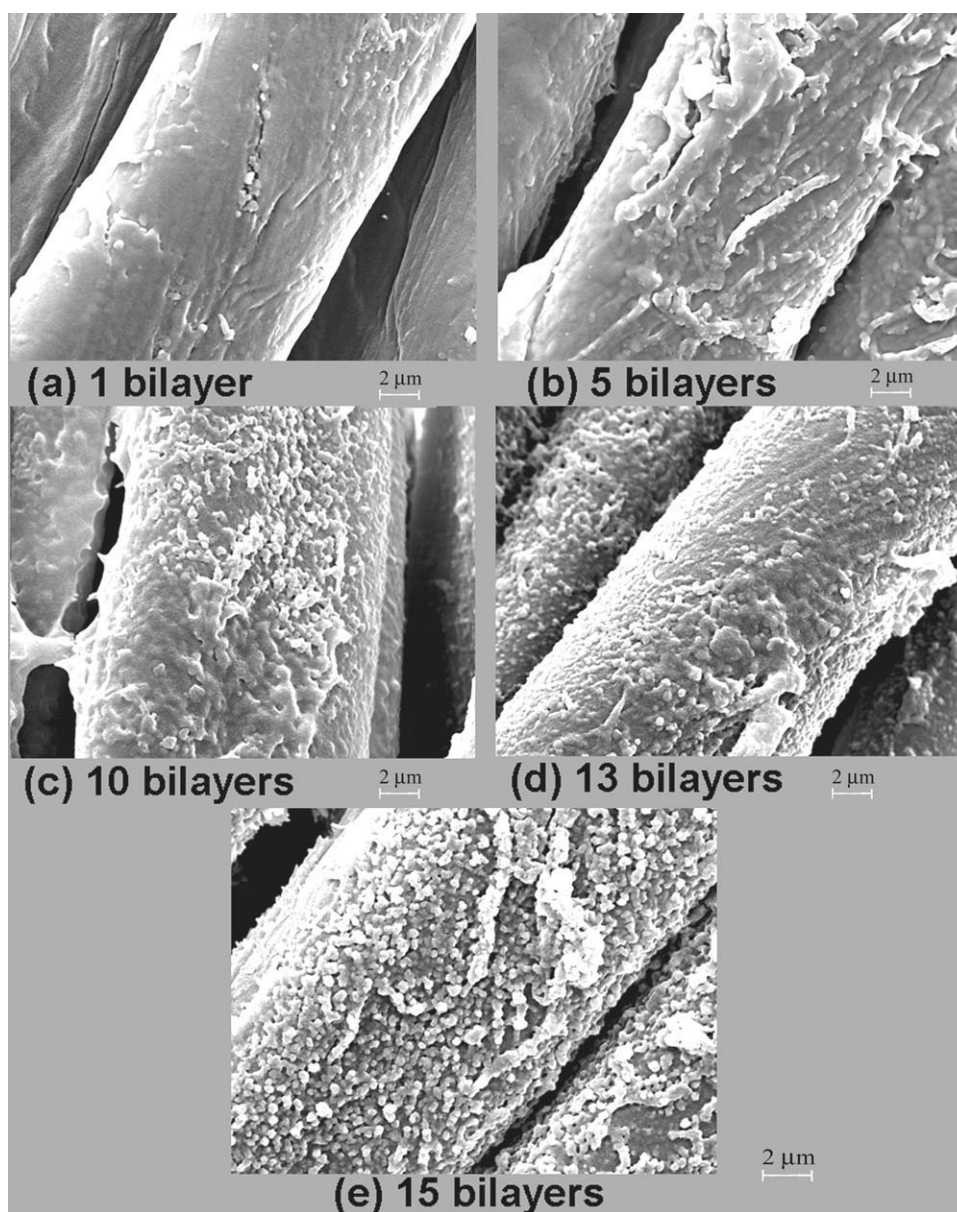


Figure 3 SEM images of cotton surfaces with different numbers of bilayers with ultrasonication (10,000 \times).

Antimicrobial activity

The antibacterial activity of the unwashed and washed samples was evaluated. Table III shows that all the unwashed samples nanocoated by PSS/chitosan experienced more than a 99% reduction of bacterial colonies versus untreated cotton. However, coated samples without any ultrasonication during rinsing with water lost a significant amount of their antibacterial activity because loosely adhering polyelectrolyte layers on the cotton substrate were washed off during the washing stage. On the other hand, ultrasonicated samples retained up to 78.6% of their

TABLE II
Air-Permeability Data

Sample	Air permeability at 100 psi (cc/cm ² /s)	CV (%)
Untreated cotton	24.5	1.05
Chitosan/PSS-nanocoated cotton (10 bilayers)	18.7	1.23
Conventional coated cotton with water-soluble PE and PVA (7%) ^a	2.5	0.98

CV = coefficient of variation; PE = chitosan polyelectrolyte; PVA = poly(vinyl acetate).

^a Thickness = 0.1 mm.

TABLE III
Antimicrobial Activity of Cotton Fabrics Coated LBL by PSS/Chitosan

Sample	Tested bacteria: <i>Staphylococcus aureus</i>					
	Unwashed samples			Washed samples		
	cfu/mL ($\times 10^8$)	Antibacterial activity (%)	CV of antibacterial activity (%)	cfu/mL ($\times 10^8$)	Antibacterial activity (%)	CV of antibacterial activity (%)
Untreated cotton	80	–	8.9	70	–	9.0
Nanocoated cotton (without ultrasonication)	1	98.7	9.2	48	31.4	7.9
Nanocoated cotton (with ultrasonication)	2	97.5	8.7	15	78.6	8.2

CV = coefficient of variation.

antibacterial activity even after washing because the loosely bound polyelectrolyte layers were removed more efficiently on account of ultrasonication in the rinsing step, and only the strongly adsorbed layers of the polyelectrolyte were retained during the subsequent deposition of bilayers. The antibacterial activity of the LBL coated cotton came from the polycationic chitosan, which was alternatively present in the multilayer structure. It is also likely that the top-most layer of the coated cotton is formed of chitosan (which is well known for its antibacterial properties),^{22–24} the free NH_3^+ groups present on the chitosan coated cotton surface in the acidic pH range interacted with the surfaces of bacterial cells and deactivated them.

CONCLUSIONS

Cotton fabric samples, which are characterized by flexibility, porosity, and relatively nonuniform surfaces, were nanocoated using a self-assembly-based LBL deposition technique with PSS/PAH and PSS/chitosan polyelectrolyte combinations. The use of ultrasonication during the intermediate washing step removed multiple loosely held polyelectrolyte layers and resulted in the uniform surface deposition of bilayers, as observed by SEM. The air-permeability data further confirmed that the deposition of LBL the layers did not block the pores of the fabric (unlike conventional coatings); therefore the original fabric handle and breathability could be retained. The retention of antibacterial activity after washing was much higher for samples for which ultrasonication was used during washing versus those for which ultrasonication was not used. The gradual change in the contact angle from hydrophilicity to hydrophobicity with the number of deposited bilayers increasing up to eight bilayers and the lack of change thereafter further indicated that the thickness of the LBL coating on the cotton fabric was

well below the micrometer range and was less than approximately 500 nm, as was also evident from SEM micrographs.

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